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In re accompanying application of)
JOHANNES P. DE JONGE ET AL)
Filed September 10, 2003)
CATALYTIC CONVERSION OF AN ORGANIC)
CARBONATE)

)

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Sir:

CLAIM TO PRIORITY

Applicants reaffirm the claim for the benefit of filing date of the following foreign patent application referred to in Applicants' Declaration:

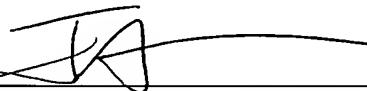
EP Application Serial No. 02256347.2 – filed August 6, 2002

A copy of the application certified by the European Patent Office is enclosed.

Respectfully submitted,

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Enclosure



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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

02256347.2

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk





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Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Catalytic conversion of an organic carbonate

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CATALYTIC CONVERSION OF AN ORGANIC CARBONATE

The present invention relates to a method for the catalytic conversion of organic carbonate, using a zinc supported catalyst and to the use of a zinc supported catalyst in such catalytic conversion method.

5 JP-A-6239806 relates to a method for the catalytic trans-esterification of alkylene carbonate with alcohol in the presence of a zinc oxide catalyst in particulate form.

10 The present invention has for its object to provide a method for the catalytic conversion of organic carbonate, having an improved conversion rate and improved yield.

15 Accordingly, the invention provides a method for the catalytic conversion of organic carbonate to the corresponding diol, wherein the organic carbonate is contacted with alcohol and/or water in the presence of zinc supported catalyst.

20 The invention is based on the insight that by the use of a catalyst having zinc in supported form the conversion rate and yield are improved, although this zinc supported catalyst may be used in an alcoholysis (reaction with alcohol) or hydrolysis (reaction with water) or in a combined hydrolysis and alcoholysis.

25 The zinc supported catalyst is a catalyst, in which the reactive zinc particles (during the reaction presumably in the form of ZnO particles) are kept apart by the support. The support can therefore consist of a material onto which zinc particles are deposited. It can

also consist of an additive that is incorporated between the zinc particles.

The zinc supported catalyst may be represented by the formula Zn/M_xAy , wherein M is a metal (such as Cr, Cu) and A is a non-metal (such as C, O, S, or a halide) and x and y may be independently 0-3. The support may comprise a material which is substantially inert in the catalytic conversion reaction or may be active in the catalytic conversion reaction. Examples of substantially inert support materials are SiO_2 , TiO_2 , ZrO_2 , Cr_2O_3 and 10 C. Examples of reactive support materials are Al_2O_3 and MgO . The zinc may also be supported in the form of a (metal) grid with other reactive and/or inert grid materials. Furthermore, the zinc supported catalyst 15 according to the invention may comprise further inert or active additives, such as Cu (CuO).

If the zinc supported catalyst comprises a support material, it is preferred to produce the zinc supported catalyst by impregnation with a zinc salt from solution 20 or from a melt. Such impregnation process will result in a zinc supported catalyst having a high catalytic activity. However, other methodologies can be adopted for depositing zinc onto a support. These include for example the precipitation of zinc salt or the gas- or liquid- 25 phase deposition of metallic or organometallic zinc species. When the impregnation is carried out using a zinc salt solution, this results in a zinc supported catalyst having the better catalyst performance.

Supported zinc catalyst can also be prepared by 30 inserting components between zinc particles, e.g. via co-precipitation or co-kneading of a zinc salt with the salt of an other metal such as chromium.

In order to obtain a zinc supported catalyst having a long-term stability and a low leaching rate (loss of metal per kg of liquid product produced), it is preferred to subject the zinc supported catalyst to calcination at 5 temperatures of 200-800 °C, preferably of 300-700 °C, more preferably of 400-600 °C.

The carbonate suitable for use in the catalytic conversion method according to the invention may be (C₁-C₈) dialkyl carbonates, wherein the alkyl groups 10 (straight, branched and/or cyclic) may be the same or different, such as methyl, ethyl, propyl and cyclohexyl; (C₅-C₉) diaryl carbonates, wherein the aryl groups may be the same or different, such as phenyl; and (C₁-C₈) alkyl (C₅-C₉) aryl carbonates or (C₅-C₉) aryl 15 (C₁-C₈) alkyl carbonates, wherein the alkyl and the aryl group are defined above; and mixtures thereof. The alkyl and/or aryl groups can be linked together to form a cyclic carbonate such as the 1,2-carbonates (alkylene carbonate) of ethylene, propylene, butadiene, cyclohexene 20 and styrene, the 1,3-carbonates of 1,3-propene diol and 1,3-butane diol, the 1,4-carbonate of 1,4-butane diol. Preferred as alkylene carbonates are ethylene carbonate and propylene carbonate.

It is noted that the alkyl group may be substituted 25 with a (C₅-C₉) aryl group (aryl alkyl group) or (C₂-C₁₀) alkylene group (alkylene alkyl group). The aryl group may be substituted with an (C₁-C₈) alkyl group (alkylaryl group) or (C₂-C₁₀) alkylene group (alkylene aryl group). The alkylene group may be substituted with an (C₁-C₈) 30 alkyl group (alkyl alkylene group) or (C₅-C₉) aryl group (aryl alkylene group). The substituents may be exemplified as mentioned above.

The alcohol may be an aromatic and/or aliphatic alcohol. The alcohol may be monohydric or polyhydric. The aliphatic alcohol comprises at least one (C₁-C₃₀) alkyl group which may be straight, branched and/or cyclic. The 5 aliphatic alcohol may be saturated or unsaturated wherein the aliphatic alcohol is saturated or unsaturated. Preferred are (C₁-C₁₀)-alkylalcohol, more preferably (C₁-C₅)alkyl alcohol or combinations thereof. Preferred are methanol and ethanol. Examples of polyhydric alcohols 10 are diols such as glycol.

An example of an aromatic C₅-C₉ alcohol is phenol.

The support material may have a pre-shaped form. This form may be globular, circular, cylinders and/or any desired or arbitrary moulded, pressed or extruded form, 15 including monolythic form or even a powder with an average particle size suitable for carrying out the reaction, such as larger than about 100 mm.

If the method according to the invention comprises a catalytic conversion by combined hydrolysis and 20 alcoholysis then generally the molar ratio between water and alcohol lies between 1:1 and 1:100, preferably between 1:5 and 1:20.

Although the method for the catalytic conversion is suitable for any dialkyl carbonate conversion, it is 25 preferred to use as a dialkyl carbonate an alkylene carbonate such as ethylene carbonate and propylene carbonate. Ethylene and propylene carbonate are most preferred. In the alcoholysis the use of methanol is preferred. The combined hydrolysis and alcoholysis in the catalytic conversion according to the method of the 30 invention results in a flexibility in the production of the corresponding diols and dialkyl carbonate together (alcoholysis) or to a production directed to the diol

predominantly or solely with the simultaneous formation and release of carbon dioxide.

5 The method and use of the catalyst according to the invention will be further elucidated by reference to the following examples, which are provided for illustrative purposes and to which the invention is not considered to be limited.

Example 1 Catalyst preparation

10 The Zn/M_xO_y catalysts were prepared by incipient wetness impregnation of SiO_2 (56 m^2/g), Al_2O_3 (287 m^2/g) or Al -stabilised MgO (53 m^2/g) with an aqueous zinc nitrate solution up to a zinc loading of 10 w%. The particles were then dried at 120 °C, calcined for 2 hours at a temperature of 450 °C and crushed to a fraction of 15 30-80 mesh.

20 $Zn.Cr_2O_3$ (Engelhard Zn-0312-T1/4) and $CuZn.Al_2O_3$ (Katalco 83-3M) catalysts were commercial catalysts, which were presumably prepared by the conventional co-kneading and co-precipitation method (see e.g. A.B. Stiles in 'Catalyst Manufacture: laboratory and commercial preparations' Dekker Inc. (1983)).

25 Catalytic testing was performed in a so-called 6 tubular nanoflow unit. This unit has 6 quartz reactors with an internal diameter of 3 mm. Each reactor was loaded with 0.15 gram of catalyst (0.2-0.6 mm diameter) that was diluted in 0.45 gram of SiC (0.05 mm diameter). 0.45 g of SiC were placed on top of this bed and used as feed pre-heater.

30 Once loaded, the catalysts were dried in situ under N_2 -flow at 120 °C and atmospheric pressure for 1 hour. The reactors were then pressurised to 25 bar and a 4:1 molar mixture of methanol and propene carbonate was fed

to the reactor at a flow rate of 5 gr/(gr cat * hr), together with a N₂ flow of 1.7 nL/(gr cat * hr).

After an initial period of 20 hours at 120 °C, the reactors were operated for 24 h, during which the liquid products were continuously condensed for off-line product analysis. The reactor temperature was then raised to 160 °C for 16 hours to simulate an enhanced deactivation and metal leaching.

Results on methanolysis

Table 1 Performance of zinc supported catalysts and reference catalysts in the methanolysis of PC (120 °C, 25 bara, WHSV= 5 gr/gr/h with MeOH: PC molar ratio of 4:1)

Catalyst	T _{calc} °C	Convers. MeOH a	PC b	Yield DMC a	MPG b	light ends b	MPC b	DMC: MPG c	Leaching d
Zn.Cr ₂ O ₃	-	12.0	16.9	7.2	15.2	0.1	1.7	0.95	0.5
CuZn.Al ₂ O ₃	-	11.4	16.5	7.6	14.6	0.2	0.0	1.04	-
10% Zn/SiO ₂	120	18.6	28.3	12.4	26.9	0.2	0.0	0.93	-
10% Zn/SiO ₂	120	20.3	31.8	12.1	28.8	0.1	3.0	0.84	2.7
10% Zn/SiO ₂	450	9.8	14.1	4.8	10.3	0.0	3.8	0.93	0.15
10% Zn/Al ₂ O ₃	120	5.1	7.5	1.8	3.7	0.0	3.7	0.95	1.8
10% Zn/Al ₂ O ₃	450	6.6	8.9	3.0	6.0	0.0	2.8	1.00	0.1

a expressed in mole% based on methanol; b expressed in mole% based on PC;

c expressed in mole:mole; d mg of metal per kg of liquid product

PC = propylene carbonate;

DMC = dimethylene carbonate;

MPG = monopropylene glycol;

MPC = methyl-propanolyl-carbonate.

The examples reported in table 1 clearly show the catalytic activity of catalysts prepared by impregnation of SiO_2 , Al_2O_3 or Al-stabilised MgO with a zinc nitrate solution. These catalysts perform better than catalysts prepared by impregnating SiO_2 with a Mg-nitrate solution,
5 which provided DMC and MPG at yields of 1.2 and 1.5 mole%, respectively, under similar conditions.

Even better catalytic performances are achieved with zinc based materials that combine a high surface area and
10 a high zinc content. This is the case for the $\text{Zn}.\text{Cr}_2\text{O}_3$ (59 w% Zn and 130 m^2/g) and $\text{CuZn}.\text{Al}_2\text{O}_3$ catalysts (22 w% Zn and 56 m^2/g). These high-surface-area zinc rich materials exhibit a catalytic activity that is comparable to that of an Al-stabilised MgO .

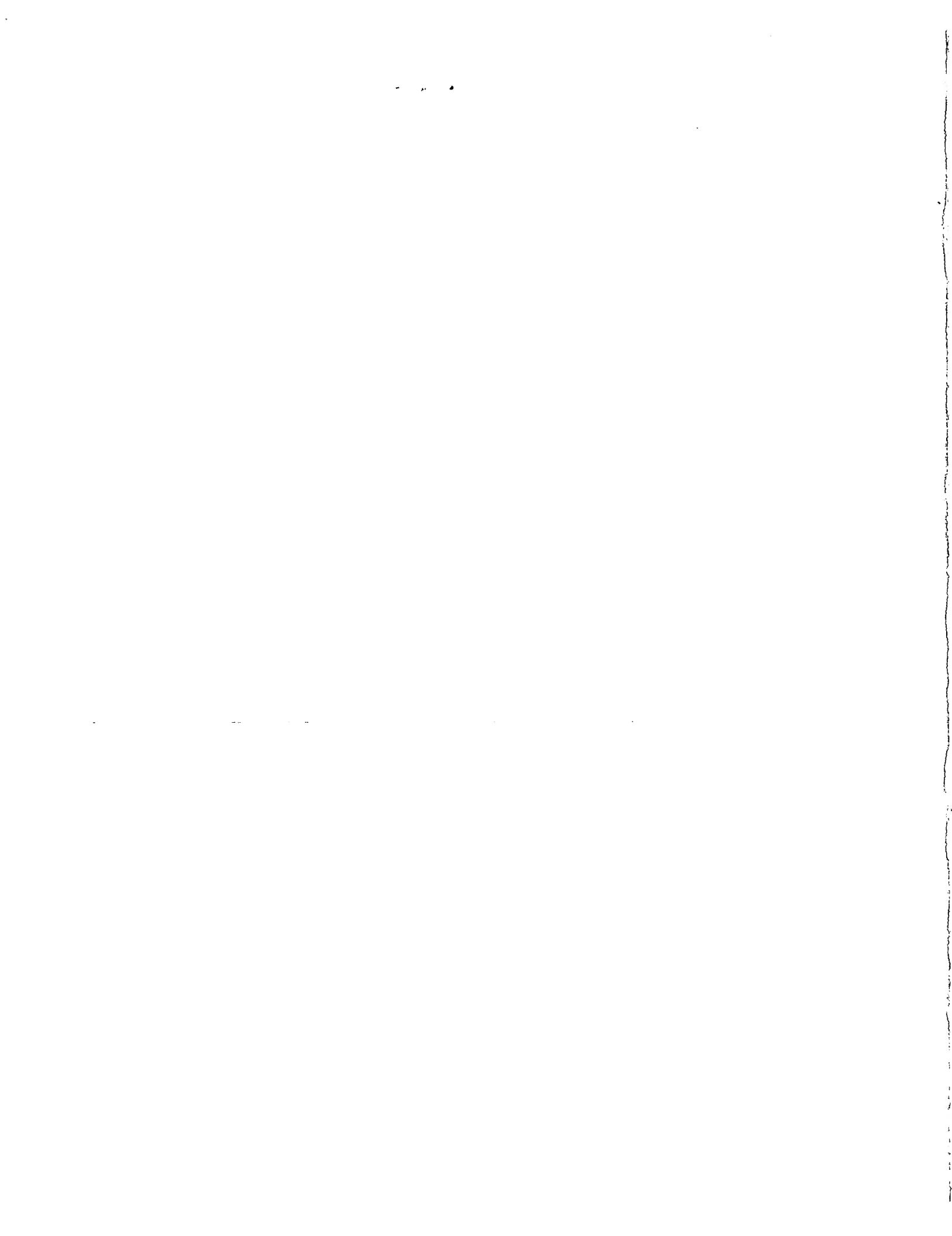
15 Furthermore, Table 1 shows that a calcination of the zinc based catalyst precursors to high temperature, e.g. 400-600 °C, is favourable for their long-term stability. It reduces the leaching rate of zinc components.

Results on hydrolysis

20 A PC-hydrolysis experiment has also been carried out with the $\text{Zn}.\text{Cr}_2\text{O}_3$ catalyst. The operation conditions were 100 °C, 25 bar and a feed consisting of a PC:water mixture of 3:1 molar ratio introduced at the higher space velocity of $\text{WHSV}=5 \text{ g/g/h}$ and a N_2 flow of 2.1 g/g/h .

25 Under these conditions, the $\text{Zn}.\text{Cr}_2\text{O}_3$ catalyst allowed a MPG yield of 15.4 mole% without formation of side products in detectable amounts. Under enhanced aging condition at 160 °C, the leaching rate of zinc species amounted to ~0.05 mg Zn/kg liquid product. For
30 comparison, a blanc experiment ran with a SiC bed allowed an MPG yield of 0.2 mole% only under these conditions.

Similar results are obtainable with the other zinc supported catalysts of the invention.



C L A I M S

1. Method for the catalytic conversion of organic carbonate to the corresponding alcohol, wherein the organic carbonate is contacted with alcohol and/or water in the presence of zinc supported catalyst.
5 2. Method as claimed in claim 1, wherein the zinc supported catalyst comprises a support material which is selected from the group comprising SiO_2 , Al_2O_3 , MgO , TiO_2 , ZrO_2 , Cr_2O_3 , C and mixtures thereof.
- 10 3. Method as claimed in claim 2, wherein the zinc supported catalyst is formed by impregnating the support material with a zinc salt or a metallic or organometallic species.
- 15 4. Method as claimed in claim 2, wherein the zinc supported catalyst is formed by co-kneading or co-precipitation of a zinc salt with the salt of an other metal.
- 20 5. Method as claimed in claims 1-4, wherein the zinc supported catalyst is calcinated at a temperature of 200-800 °C, preferably of 300-700 °C, more preferably of 400-600 °C.
6. Method as claimed in claims 1-5, wherein the alcohol is selected from an aromatic (C₅-C₉) alcohol and/or aliphatic C₁-C₃₀ alcohol.
- 25 7. Method as claimed in claim 6, wherein the aromatic alcohol is phenol.
8. Method as claimed in claim 6, wherein the aliphatic alcohol is saturated or unsaturated C₁-C₁₀-alkylalcohol, preferably C₁-C₅ alkyl alcohol or combinations thereof.

9. Method as claimed in claims 1-8, wherein the organic carbonate is a dialkyl carbonate, diaryl carbonate, alkylaryl carbonate, arylalkyl, wherein the alkyl and/or aryl groups can be linked together such as in alkylene carbonate.

5

10. Use of a zinc supported catalyst as defined in claim 1 for the alcoholysis of an organic carbonate.

11. Use of a zinc supported catalyst as defined in claim 1 for the hydrolysis of an organic carbonate.

10 12. Use of a zinc supported catalyst as defined in claim 1 for the combined alcoholysis and hydrolysis of an organic carbonate.

A B S T R A C T

CATALYTIC CONVERSION OF AN ORGANIC CARBONATE

Method for the catalytic conversion of organic carbonate to the corresponding alcohol, wherein the organic carbonate is contacted with alcohol and/or water in the presence of zinc supported catalyst.

